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Supramolecular Nanodevice Based on Helical Encapsulation of Photo/Electroactive Oligomers

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Summary: Oligophenylenevinylene (OPV)-based A-D-A chain chromophores were synthesized by symmetrically linking electron- or energy-acceptor units through an alkyl spacer. Phto-induced thru-space electron/energy-transfer (eT/ET) was investigated in the presence and absence of amylose encapsulation with respect to the spacer length (D-A distance) and acceptor strength. Fluorescence quenching of the D-A chromophores suggests that with the helical encapsulation, eT/ET have a discrete D-A distance dependence while the free chromophores have mixed contributions, some from eT but largely from self-quenching due to aggregation and/or solvent deactivation.

Keywords: energy/electron transfer; helical amylose; oligomer; supramolecule

Introduction

There have been made numerous types of molecular devices to develop enhanced sensitivity and efficiency in sensing/monitoring, switching/processing and energy/electron-transport systems. They are architectured either by covalent bonding or noncovalent bondings such as H-bonding, electrostatic, dipolar, π-π and steric interactions in a systematic and controlled manner. The non-covalent means are the basic elements for constructing supramolecular devices, so that diverse applications are possible for integrating structures and thus, versatile new functional properties.[1,2]

We have developed a unique supramolecular nanodevice to develop high efficiency energy/electron-transfer (ET/eT) properties mimicking the photosynthetic reaction center by encapsulating a donor-acceptor (D-A) chain chromophore with a helix-forming polymer, amylose.[3–6]

It has been known that ET/eT is D-A distance dependent while a long-lived charge-separated state requires a remote separation of D-A moieties. Such a conflicting molecular situation has to be resolved by a new device concept. The key is to make the ET/eT rates very fast over a long distance at a minimal energy loss. Nonetheless, the geometrical distance of D-A does not have much meaning unless the conformational flexibility is controlled. An elegant solution was made to rigidify the chromophor using rigid linkers between the chromophoric units and proved a significant effect.[7] However, there still needs a remedy for energy loss in the transport of energy/electrons, occurring due to unwanted excited-state quenchings such as by aggregation and environmental deactivation.

All these problems can be resolved simultaneously by a supramolecular architecture that is based on a helical encapsulation of chromophores that we have developed.[8,9] Of the advantages gained by encapsulation of the chromophores, the most notable one is the large enhancement of the fluorescence quantum yield, which results from single molecular confinement in the rigid and quenching-free environment. A distinctive feature of the supramolecular system is the formation of oriented self-assembly thin films upon casting a solution since amylose alone is unable to do it.[6]

Herein, we discuss highly efficient, one-dimensional ET/eT properties of amylose-encapsulated D-A chromophores along the helical channel.

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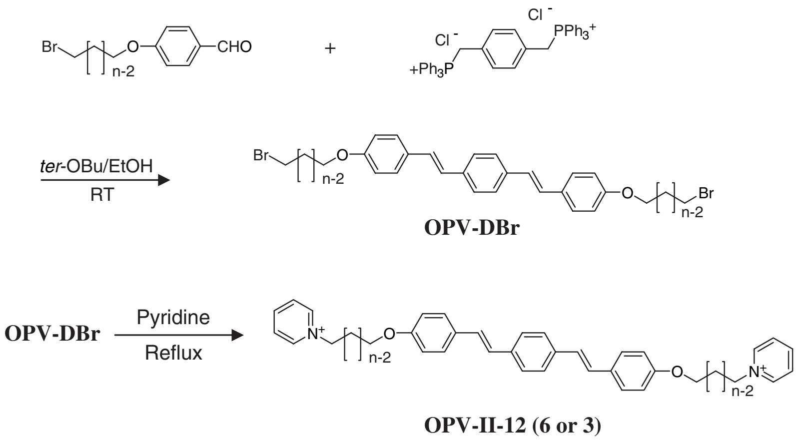
Materials, Processing and Measurements

Materials

The general procedure for the synthesis of OPV-II-, OPV-III- and OPV-IV- series chromophores is as shown in the Scheme (below): A mixture of 4-hydroxybenzaldehyde (0.1 mole) and potassium carbonate (0.15 mol) in 100 ml DMF was treated with ω,ω′-dibromoalkane (0.3 mole) in 20 ml DMF at RT, diluted with water and extracted with methylene chloride. The product (ω-bromoalkyl benzaldehyde) was separated by a silica gel column chromatography (20% yield). The bromoalkyl benzaldehyde was mixed with *p*-xylene bis(triphenylphosphonium bromide in 100 ml ethanol and then, treated with *ter*-butoxide with stirring, 5 hrs at RT. The precipitates were filtered, washed with water and then ethanol. The yellowish solid was dissolved in pyridine, *o*-xylene solutions of N-alkylbipyridine and N,N-dimethylaminostyryl-*p*-pyridine, respectively and refluxed for two days to obtain precipitates of OPV-II, OPV-III and OPV-IV derivatives, respectively. Amylose (a linear chain polymer consisting of 4-α-D-glucose) is a commercila product (Aldrich, Mw ≈ 60 kDa).



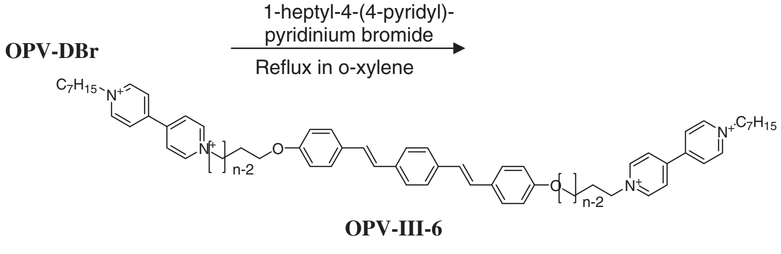
Processing

Helical encapsulation of chromophores with amylose was processed in water or water-DMSO mixtures according to the procedure reported by us and determined by using absorption and fluorescence spectral changes.[8]

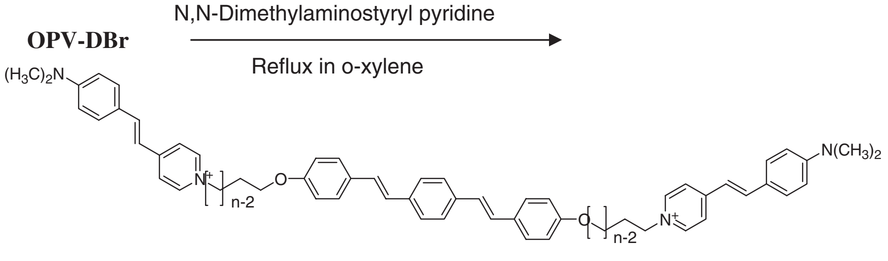
Measurements

Absorption and fluorescence spectra were recorded using Cary UV-Vis-NIR spectrometer (Varian) and DN3000 Fluorescence Fluorometer (SPEX), respectively.

OPV-II-12: ^{1}H-NMR (400MHz, DMSO-D$_6$): 9.09 (4H, d, 5.5), 8.61 (2H, t, 7.8), 8.16 (4H, m), 7.55 (4H, s), 7.53 (4H, d, 8.8), 7.21 (2H, d, 16.6), 7.09 (2H, d, 16.4), 6.93 (4H, d, 8.7), 4.59 (4H, t, 7.4), 3.98 (4H, t, 6.4), 1.91 (4H, m), 1.71 (4H, m), 1.41 (4H, m), 1.25 (28H, m).



OPV-III-6: ^{1}H-NMR (300MHz, DMSO-D$_6$): 9.411 (8H/0.98), 8.81 (8H/1.12), 7.56 (4H/0.75, s), 7.53 (4H/0.75), 7.21 (2H/0.4, d, 22), 7.08 (2H/0.4, d, 22), 6.93 (4H/0.76, d, 10.8), 4.7 (8H/1.14, m), 3.9 (4H/0.79, m), 2.05~0.883 (36H/9.66, m).



OPV-IV-10

OPV-IV-10: ^{1}H-NMR (400MHz, DMSO-D$_6$): 8.82 (4H, d, 5.4), 8.10 (4H, t, 5.1), 7.9 (2H, d), 7.6~7.5 (12H, m), 7.4~7.1 (6H, m), 7.00 (4H, d, 8.6), 6.82 (4H, d, 7.4), 4.45 (4H, t), 4.01 (4H, t), 3.1 (12H, s), 1.9 (4H, m), 1.7 (4H, m), 1.3 (24H, m).

Results and Discussion

A series of bidirectional A-D-A chain chromophores based on OPV (D) with various acceptors (As), such as pyridinium, viologen and *p*-dimethylamonostyryl-4-alkyl pyridinium (DASP), and alkyl-spacers (C_n) have been synthesized as shown above. Helical encapsulation of the chromophores with amylose is evidenced by red-shift of absorption maximum, enhanced fluorescence intensity and a marked circular dichroism (CD). The extent of ET/eT, which depends on the encapsulation, D-A distance, D/A strength and local environment, was determined based on the degree of the fluorescence quenching of D due to the presence of A in aqueous solutions.

Spectroscopic Evidence for Helical Encapsulation

Absorption spectra (Figure 1, *left*) indicate that the encapsulation of OPV-II-12 dye by helical amylose advances proportionately with increasing amylose concentration, reaching saturation when the amylose concentration (where the molar concentration is based on polymer repeat units) is 100 times relative to the dye. Exactly the same trend is reproduced by fluorescence intensity (Figure 1, *right*). From this, it is assumed that each amylose helix includes only one dye molecule. A further evidence for the helical encapsulation is demonstrated by the circular dichroism (CD) spectrum (Figure 2). This is an induced Cotton effect from the chromophore encapsulated with helical amylose, which split the absorption band of the dye into two CD peaks of opposite sign, changing form negative to positive Cotton effect at the absrption maximum, indicative of a left-handed helix.[10]

Energy- and Electron-Transfer

Figure 3 shows electron- (*left*) and energy-transfer (*right*) of OPV-III-6 and OPV-IV-10, respectively. This is is assessed based on the decrease in the fluorescence intensity of OPV (D) due to the presence of A. For ET to occur in OPV-IV-10, the emission band of OPV ($\lambda_{em} = 425$ nm) should overlap with the absorption band of DASP (A) ($\lambda_{max} = 475$ nm).

For OPV-IV-10 (*right*), the initial OPV fluorescence is nearly completely quenched ($> 99\%$) by the DASP unit (A) upon excitation of the OPV unit, and the subsequent ET excitation of the DASP unit brings about a large enhancement ($> \times 10$) in DASP fluorescence ($\lambda_{em} = 620$ nm). A Förster-type calculation using a

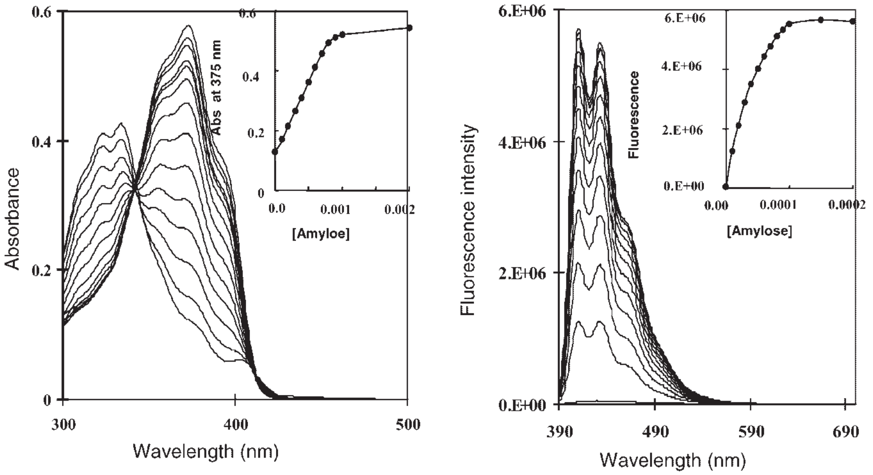


Figure 1.

Changes in absorption and fluorescence (Ex. at 375 nm) spectra of OPV-II-12 upon titration of amylose in water (1% DMSO in water): $[\text{OPV-II-12}] = 1.0 \times 10^{-5}$ M for absorption and 1.0×10^{-6} M for fluorescence spectra; $[\text{amylose}] = 0$ to 2.0×10^{-3} M.

dyad model confirms the efficient ET observed experimentally.

On the other hand, the free OPV-III-6 (without amylose), shows a much larger decrease in the OPV fluorescence intensity (at 432 nm), compared to that of the encapsulated counterpart (vide supra). Similarly but for different reasons, the encapsulation-free OPV-IV-10 also exhibits an extremely low OPV emission intensity (at 432 nm) relative to the encapsulated counterpart. The former (OPV-III-6) may be due to conformational flexibility in water, which promotes collisional quenching, and the latter (OPV-IV-10) is due to a dominant aggregation, such that there is no measurable differences in the intensity by exciting either OPV (at

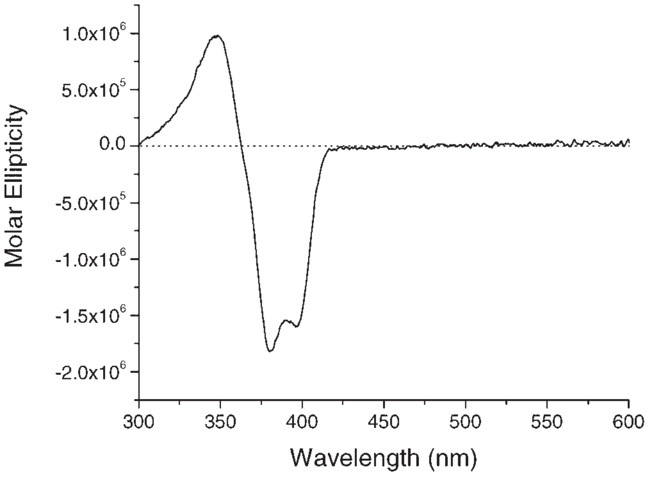


Figure 2.

Induced circular dichroism (ICD) spectrum of OPV-II-12 encapsulated by amylose helix; $[\text{OPV-II-12}] = 1 \times 10^{-5}$ M and $[\text{amylose}] = 1 \times 10^{-3}$ M in water.

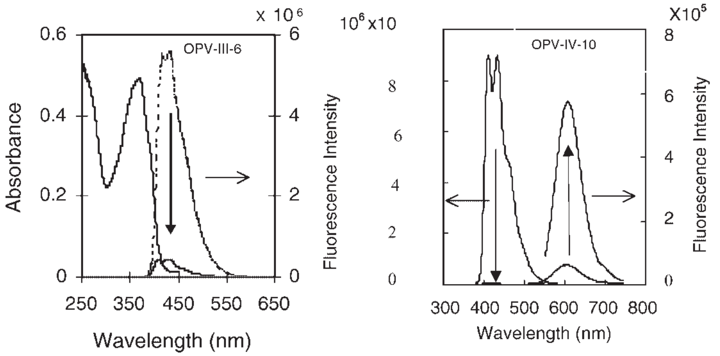


Figure 3.
Electron- and energy-transfer in helically encapsulated OPV-based chromophores by excitation of OPV unit (D) at 375 nm: (*left*); Decrease in fluorescence intensity of OPV unit in OPV-III-6 due to eT to viologen moiety (A) from OPV unit (represented by OPV-II-12) in water; [OPV-III-6]/[Amylose] = 1×10^{-5} M/1×10^{-3} M for ABS and 1×10^{-6} M/1×10^{-4} M for FL spectra, and (*right*); Fluorescence quenching of OPV and concomitant enhanced fluorescence intensity of DASP unit (A) in OPV-IV-10 due to ET from OPV unit (D) in 25% DMSO; [OPV-IV-10] = 1×10^{-5} M, [Amylose] = 1×10^{-3} M.

370 nm) or DASP itself (at 480 nm). These clearly suggest that the unusually low fluorescence intensities (of OPV) for the free OPV-III-6 and the free OPV-IV-10 are not the result of a complete eT/ET. In this regard, it is particularly significant for the encapsulated counterpart to observe a well-defined photo-induced eT with a remarkable efficiency over the distance of 10 Å or more.

Compared to OPV-III-6, the extent of fluorescence quenching (due to eT) of OPV-II-6, for example, is much smaller due to the weak A strength. Nonetheless, the weakness of the A strength can make the degree of eT more distinguishable by D-A distance. Particularly, the facile encapsulation with helical amylose makes OPV-II-series chromophores more attractive for studying the distant dependence. As

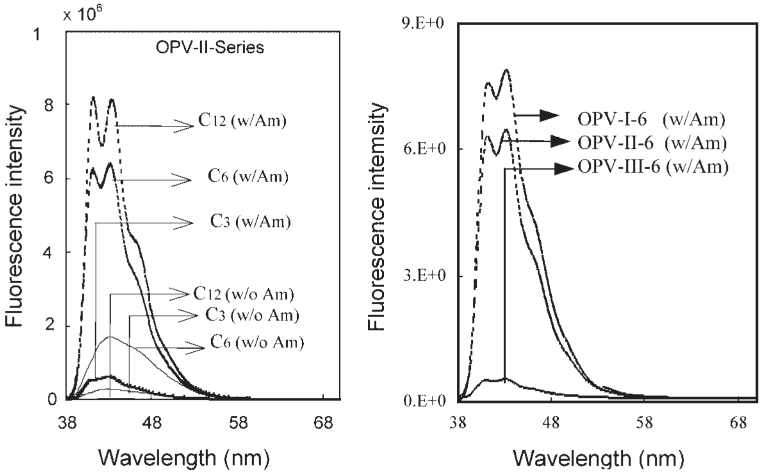


Figure 4.
Dependence of fluorescence quenching (due to eT): (*left*); on D-A distance (Cn) of OPV-II chromophores (with and without amylose) and (*right*); on A-strength of OPV-based chromophores with a spacer length C6: A-strength; III (Viologen) > II (Pyridinium) > I (triethylammonium). [Chromophore] = 1×10^{-5} M, and [amylose] = 2×10^{-3} M, in water.

shown in Figure 4, *left*, the eT of OPV-II chromophores, when encapsulated, exhibit a strong dependence on the spacer length, indicating that the chromophore with C_3 spacer has the largest eT (decrease in the fluorescence intensity), and the one with C_{12} has a negligible eT.

It was further confirmed (Figure 4, *right*) that the eT of the encapsulated chromophores strongly depends on the A strength; ammonium < pyridinium, < viologen. In contrast, the eT quenching for the encapsulation-free counterparts has mixed contributions from both the distance effect and non-radiative deactivation by aggregation and/or collisional quenching.[11] These are closely related to the environmental sensitivity of the free chromophores and are reflected in their low fluorescence quantum yields[4] and very short lifetimes,[4] particularly for the encapsulation-free OPV-II-12 due to a strong aggregation. On the contrary, the electronic coupling of the D-A chromophores confined in the amylose helix is little affected by local environment, so that one-dimensional event of transport prevails.

Conclusion

Fluorescence quenching of the helically-encapsulated D-A chromophores is dominated by photo-induced eT/ET with a well-defined distance effect and A strength, whereas the free chromophores have mixed contributions from some eT but largely from self-quenching due to aggregation, solvent deactivation and conformational flexibility.

[1] J.-M. Lehn, "*Supramolecular Chemistry*", VCH, New York **1995**.

[2] V. Bazani, M. Venturi, A. Credi, "*Molecular Devices and Machines*", Wiley-VCH, Weinheim **2003**.

[3] O.-K. Kim, J.-T. Je, G. Jernigan, L. Buckley, D. Whitten, *J. Am Chem. Soc.* **2006**, *128*, 510.

[4] O.-K. Kim, J.-T. Je, J. S. Melinger, *J. Am. Chem. Soc.* **2006**, *128*, 4532.

[5] M. Pepitone, J. Melinger, G. Jernigan, O.-K. Kim, *Organic Lett.* Submitted.

[6] G. Jernigan, M. Pepitone, J. Melinger, O.-K. Kim, Unpublisher result.

[7] T. D. M. Bell, T. A. Smith, K. P. Ghiggino, M. G. Ranasinghe, M. J. Shephard, M. N. Paddon-Row, *Chem. Phys. Lett.* **1997**, *268*, 223.

[8] O.-K. Kim, L.-S. Choi, *Langmuir*, **1994**, *10*, 2842.

[9] O.-K. Kim, L.-S. Choi, H.-Y. Zhang, X.-H. He, Y.-H. Shih, *J. Am. Chem. Soc.* **1996**, *118*, 12220.

[10] "*Circular Dichroism-Principle and Applications*", 2nd ed., N. Berova, K. Nakanishi, R. W. Woody, Eds., Wiley-VCH: New York, 2000; Chapter 12.

[11] J. R. Lakowicz, "*Principle of Fluorescence Spectroscopy*", 2nd ed., Kluwer Academic/Plenum Publishers, New York, 1999, Chapters 8 and 14.